Manuscript to be submitted as a Letter to *Nature*

Title: Black carbon in estuarine (coastal) high-molecular-weight dissolved organic matter

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Abstracts for Manuscript Review

Scientific

Dissolved organic matter (DOM) in the ocean constitutes one of the largest pools of organic carbon in the biosphere, yet much of its composition is uncharacterized. Observations of black carbon (BC) particles (by-products of fossil fuel combustion and biomass burning) in the atmosphere, ice, rivers, soils and marine sediments suggest that this material is ubiquitous, yet the contribution of BC to the ocean's DOM pool remains unknown. Analysis of high-molecular-weight DOM isolated from surface waters of two estuaries in the northwest Atlantic Ocean finds that BC is a significant component of DOM, suggesting that river-estuary systems are important exporters of BC to the ocean through DOM. We show that BC comprises 4-7% of the dissolved organic carbon (DOC) at coastal ocean sites, which supports the hypothesis that the DOC pool is the intermediate reservoir in which BC ages prior to sedimentary deposition. Flux calculations suggest that BC could be as important as vascular plant-derived lignin in terms of carbon inputs to the ocean. Production of BC sequesters fossil fuel- and biomass-derived carbon into a refractory carbon pool. Hence, BC may represent a significant sink for carbon to the ocean.

General

Black carbon material, by-product of fossil fuel combustion and vegetation burning, is present in the atmosphere, soils, ice, rivers, coastal ocean particles and ocean sediments. Our work presents the first published measurements of black carbon material in dissolved matter within the ocean. The contribution of black carbon to the Atlantic Ocean from Delaware Bay and Chesapeake Bay along the U.S. coast suggests that global inputs of black carbon to the ocean are likely to be significant. Black carbon in dissolved matter within the ocean represents a previously unknown carbon reservoir and sink.

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June 4, 2003

Philip Campbell
Editor, *Nature*
The Macmillan Building
4 Crinan Street
London N1 9XW, UK

Dear Dr. Campbell,

I respectfully submit the attached manuscript entitled, "Black carbon in estuarine (coastal) high-molecular-weight dissolved organic matter", for publication as a letter to *Nature*. The manuscript presents distributions of black carbon within the dissolved organic matter (DOM) pool along two estuaries and adjacent coastal ocean in the Mid-Atlantic U.S. The results presented are unique because no other published measurements of black carbon within DOM exist for oceanic environments. The work demonstrates that BC contributions to the ocean from river-estuary systems can be substantial and reveals how these novel measurements may influence our understanding of the ocean's carbon cycle.

Summaries

Significance of work to *Nature* readers

Currently, there are no known published measurements of black carbon (BC) concentrations within the dissolved organic matter pool (DOM) in oceanic environments. Production of BC sequesters fossil fuel- and biomass-derived carbon into a refractory carbon pool, and may represent a significant carbon sink into the ocean. Analysis of high-molecular-weight DOM from two estuaries and the adjacent coastal ocean demonstrates that BC is a significant component of DOM, and suggests that river-estuary systems are important exporters of BC to the ocean through DOM. Our results show that BC comprises 4-7% of the dissolved organic carbon (DOC) at coastal ocean sites, which supports the hypothesis that the DOC pool is the intermediate reservoir in which BC ages prior to sedimentary deposition. Furthermore, our calculations suggest that BC fluxes into the ocean may exceed the inputs of carbon from vascular plant-derived lignin.

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Summaries

Explanation of conclusions at understandable level the for the public

Black carbon material, by-product of fossil fuel combustion and vegetation burning, is present in the atmosphere, soils, ice, rivers, coastal ocean particles and ocean sediments. Our work presents the first published measurements of black carbon material in dissolved matter within the ocean. The contribution of black carbon to the Atlantic Ocean from Delaware Bay and Chesapeake Bay along the U.S. coast suggests that global inputs of black carbon to the ocean are likely to be significant. Black carbon in dissolved matter within the ocean represents a previously unknown carbon reservoir and sink.

Sincerely,

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Dr. Antonio Mannino
Oceanographer

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Black carbon in estuarine (coastal) high-molecular-weight dissolved organic matter

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Dissolved organic matter (DOM) in the ocean constitutes one of the largest pools of organic carbon in the biosphere, yet much of its composition is uncharacterized. Observations of black carbon (BC) particles (by-products of fossil fuel combustion and biomass burning) in the atmosphere, ice, rivers, soils and marine sediments suggest that this material is ubiquitous[1-4], yet the contribution of BC to the ocean's DOM pool remains unknown. Analysis of high-molecular-weight DOM isolated from surface waters of two estuaries in the northwest Atlantic Ocean finds that BC is a significant component of DOM, suggesting that river-estuary systems are important exporters of BC to the ocean through DOM. We show that BC comprises 4-7% of the dissolved organic carbon (DOC) at coastal ocean sites, which supports the hypothesis that the DOC pool is the intermediate reservoir in which BC ages prior to sedimentary deposition[5]. Flux calculations suggest that BC could be as important as vascular plant-derived lignin in terms of carbon inputs to the ocean. Production of BC sequesters fossil fuel- and biomass-derived carbon into a refractory carbon pool. Hence, BC may represent a significant sink for carbon to the ocean.

Black carbon represents a refractory and chemically heterogeneous product of incomplete combustion from biomass burning and fossil fuel combustion. BC is defined as a "continuum of partly charred plant material through char and charcoal to graphite and soot particles recondensed from the gas phase[6]." Sources of BC to the ocean include atmospheric deposition of land-derived BC aerosols, river-estuary transported material and exhaust from marine diesel engines. Most BC is deposited locally, but long-range transport through rivers and the atmosphere is possible. Submicron particles of BC can remain in the atmosphere for long periods (40 hours to 1 month) and reach remote ocean regions[1,7]. BC comprises 10-50% of sedimentary organic carbon[8,9] and is much older (2400 to 13,900 years older) than non-black carbon material in deep ocean sediments[5]. An unresolved issue is whether the BC that ultimately resides in marine sediments (estimated at 2.4-6 x 10^{18} g C)[10] ages within the ocean as DOC or in soils[5].

In an effort to understand the importance of riverine and estuarine DOM as a source of black carbon to the ocean, the BC component of ultrafiltered high-molecular-weight DOM (UDOM) was measured in surface waters of the Delaware Estuary and Chesapeake Bay (mid-Atlantic, USA) on multiple cruise opportunities[11,12]. Black carbon yields in estuarine UDOM varied substantially over space and time from 4.6 to 72% BC/UDOM-C (27 ± 17%; mean ± sd; Fig. 1a). Distributions of BC concentrations in UDOM ranged from 45 to 1038 μg BC l^{-1} across the salinity gradient (Fig. 1b). The spatial and seasonal distributions of BC along the salinity gradient of Delaware Bay suggest that the higher levels of BC in surface water UDOM originated from localized sources, possibly from atmospheric deposition or released from resuspended sediments. The highest and most variable BC concentrations and yields were observed within the turbid region of Delaware Bay (110 to 50 km upstream from the bay mouth). The turbid region is immediately downstream from the city of Philadelphia, and its coastline bears substantial industrial and urban activity[13].

The highest levels of BC in UDOM occurred during periods of lower discharge of the Delaware River (average daily mean discharges for the Delaware River at Trenton, New Jersey for the 30 days prior to sampling cruise: 491 $m^3 s^{-1}$ for May-June 1996, 147 $m^3 s^{-1}$ for August-September 1996, 500 $m^3 s^{-1}$ for February-March 1997, and 272 $m^3 s^{-1}$ for May-June 1997)[14]. Higher river discharge in June 1996 and March 1997 likely diluted and transported the localized inputs of BC near the 100 km site to areas further downstream (Fig. 1). At the Delaware River site, BC concentrations were modestly higher (125 ±32 μg BC l^{-1}) than values observed in the coastal ocean (93.8 ±10.9 μg BC l^{-1}; Table 1). The Chesapeake Bay sites contained higher levels of BC than observed at analogous sites along the Delaware Estuary. BC concentration was nearly three times higher (283 μg l^{-1}) at the freshwater site in Chesapeake Bay than observed at the Delaware River site (Table 1).

With the exception of lower BC content at sites where salinity <1 psu, BC concentrations and yields in UDOM declined along the salinity gradient from the turbid region to the coastal ocean of the Delaware Estuary (Fig. 1). Least squares regression analyses revealed a significant relationship between Delaware Bay black carbon and salinity for samples collected at sites where salinity >1 psu (Table 1). The relationship was not significant when all data points from the Delaware Estuary transect were included in the regression analysis ($r^2 < 0.1$, $P > 0.1$). The apparent localized sources of BC in the mid-estuary region introduced BC into surface water UDOM, which was then diluted downstream as bay water mixed with Atlantic Ocean water.

To determine whether the BC in UDOM was derived from fossil fuel combustion and/or biomass burning, radiocarbon dating was conducted on a sub-set of UDOM-BC samples from the Delaware Estuary and Chesapeake Bay sites (measured at the National Ocean Sciences Accelerator Mass Spectrometry facility at WHOI). Potential contamination of samples with bomb ^{14}C was a concern, because samples were not collected and processed with the intent to measure $\Delta^{14}C$. Most of the BC samples had radiocarbon ages of modern to greater than modern, and contamination of those samples with non-BC ^{14}C cannot be dispelled with certainty. Contamination of only a few molecules of ^{14}C-labeled material is needed to distort radiocarbon age measurements. However, BC collected downstream of the Chesapeake Bay mouth had a radiocarbon age of 29,400 years old and $\delta^{13}C$ of -46.2‰, which supports a fossil fuel source for BC at that site. Such findings demonstrate how anthropogenic activity can impact the age of DOC in the ocean, particularly in ocean regions with high levels of BC aerosol deposition.

Standard reference materials of BC and standard matrices composed of natural organic matter similar to DOM (but with no expected BC content) were examined (1) to permit comparison of our BC measurements with other published BC measurements and (2) to determine whether the thermal oxidation procedure (see Methods) yielded extraneous BC. Diesel particulate material (NIST SRM 1650) and urban dust (NIST SRM 1649a) contained BC levels (0.52 and 0.041 g BC/g dry weight, respectively; Table 2) comparable to previously published values[8,15,16]. Results from natural organic matter comparable in composition to DOM suggest that little to no extraneous BC was produced during analysis. Thermal oxidation produced no extraneous BC in Suwannee River DOM (0.34% BC/TOC), peat humic acid (0.06%) and virtually no BC for *Skeletonema costatum* detritus (0.82%; Table 2). When thermal oxidation was conducted after acid fuming, higher amounts of extraneous BC were detected in *S. costatum* detritus (2.32%). Acid-labile biochemicals present in diatom detritus may have produced the artifact material during thermal oxidation. To eliminate this possibility, samples and reference materials were fumed with acid vapors after thermal oxidation. A small amount of extraneous BC was measured from actively growing phytoplankton cultures of *Isochrysis galbana* (2.33%) and *S. costatum* (4.68%). Similar level of extraneous BC (3.75% BC/TOC) was found in a culture of *Thalassiosira* *weissflogii*[15]. Thermal oxidation of calcium carbonate (0.2% BC/total carbon) did not produce BC artifacts. Such low levels of BC artifacts in natural organic matrices compared to the high BC yields in UDOM samples (Fig. 1a) suggest that production of BC artifacts had minimal impact on our BC measurements of UDOM.

The BC found in UDOM was likely derived from deposition of ultra-fine soot aerosols and/or material that shed or desorbed from suspended particles. Aerosols derived from urban-industrial pollution and biomass burning each contain a sub-micron size mode (<0.1 to <1 μm) and a coarser mode (1 to 10 μm)[17]. Atmospheric deposition of BC aerosols must also contribute BC to high-molecular weight DOM and suspended particles in the open ocean as well as coastal regions. For example, aerosols produced from biomass burning in southern Africa are transported at least 4000 km into the South Atlantic[18]. Currently, there are no known previously published measurements of black carbon concentrations for DOM in the ocean. One report alludes to an unpublished measurement of BC within high-molecular-weight DOM at a site in the North Pacific Ocean, where BC comprised 8% of total organic carbon[15]. In our study, BC comprised substantial portions of DOC (4-7%) in the coastal ocean adjacent to Delaware Bay and Chesapeake Bay. The annual flux of BC from Delaware Bay UDOM to the Atlantic Ocean was estimated at $2.37\times10^{10} \pm 0.27\times10^{10}$ g BC yr^{-1} (Table 3), illustrating the potential significance of estuarine contributions of BC to the ocean. Extrapolating BC concentrations in UDOM from the Delaware River and headwaters of Chesapeake Bay (156.4 ± 76.0 μg l^{-1}) to estimate the flux of BC within DOM through world rivers yields a global river flux of $5.52 \pm 2.68 \times10^{12}$ BC yr^{-1}. Comparisons of BC and lignin (biopolymer of vascular plants) fluxes to the ocean suggest that the flux of black carbon to the ocean through DOM may be greater than the flux of lignin (Table 3). The presence and magnitude of BC within the DOC pool supports the hypothesis that the DOC pool represents the reservoir in which BC ages prior to deposition to deep ocean sediments[5].

Thermal oxidation yields primarily the soot component of BC and is less effective for quantifying char-type BC, which is more thermally labile than soot or graphite BC[15,23,24]. Hence, our measurements of BC within DOM constitute only a portion of the BC continuum and are probably underestimates of the total BC content within coastal DOM. Suspended particles in coastal and open ocean regions may contribute even greater quantities of BC. For example, the flux of BC in suspended particles from the Mississippi River to the Gulf of Mexico was estimated at 5 x 10^{11} g BC yr^{-1} (ref. 4). Biomass burning and combustion of fossil fuels have increased over the past century with uncertain impacts on the Earth's climate and on biogeochemical cycles. Production of BC sequesters fossil fuel- and biomass-derived carbon into a biologically refractory carbon pool. Thus, BC may represent an important sink for carbon into the ocean. The distribution of BC within DOM and suspended particles in the ocean needs to be examined further to ascertain the significance of BC in the ocean's carbon cycle.

Methods

Size-fractionated DOM was collected at 5 to 7 sites along the salinity gradient from the Delaware River to the coastal ocean in June 1996, September 1996, March 1997 and May-June 1997[11,12]. Samples from the headwaters of Chesapeake Bay and beyond the Chesapeake Bay mouth were also collected in May-June 1997. DOM (<0.2 μm) was separated into three nominal size fractions (< 1 kiloDalton [kDa], 1-30 kDa and 30 kDa-0.2 μm) by tangential flow ultrafiltration[11]. The two high-molecular-weight fractions were concentrated and desalted during ultrafiltration. BC was measured only in the 1-30 kDa fraction (UDOM), which comprised on average 35±15% of DOC[12]. The 30 kDa-0.2 μm fraction typically comprised only 1-3% of DOC.

Lyophilized UDOM samples were weighed into silver capsules and thermally oxidized within a muffle furnace at 375°C in the presence of air for 24 hours[8]. Thermally oxidized and non-thermally oxidized samples were acidified with 12 M HCl vapors for 48 hours, oven dried (45-55°C) and analyzed for carbon content using a CHN elemental analyzer.

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Figure 1. Distributions of black carbon (a) yields and (b) concentrations in UDOM from the Delaware Estuary. Closed circle – Delaware June 1996, closed square – Delaware September 1996, open triangle – Delaware March 1997, open circle – Delaware May-June 1997 and closed triangle – Chesapeake Bay May-June 1997 (panel b only). Error bars represent 1 standard deviation for triplicate or duplicate analyses.

Table 1. Black Carbon content in UDOM across salinity regions in the Delaware Estuary and Chesapeake Bay sites and least squares regression analyses of Delaware Estuary BC versus salinity >1 psu.

	Salinity	BC	BC/UDOM-C	BC/DOC
	(psu)	(μg/L)	(%)	(%)
Delaware River	0.097	125	12.2	5.4
	±0.020*	±32	±3.5	±1.9
Delaware Turbid	5.0	448	38	14.0
Region	±4.5	±331	±25	±9.2
Delaware Lower	20.9	192	26.4	8.0
Estuary	±4.6	±83	±9.8	±2.5
Coastal Ocean	30.02	93.80	21.49	5.52
	±1.17	±10.87	±4.05	±1.03
Chesapeake Bay	0.492	282.92	33.16	12.744
headwaters		±1.49†	±0.18†	±0.067†
Chesapeake Bay	23.76	161.8	26.3	7.06
coastal ocean		±13.5†	±2.2†	±0.59†

Linear Regressions for sites where salinity >1 psu

	X	Y	Y	Y
Data Transformation	none	$[\mathrm{Log}_{10}(Y)]^{0.5}$	$(Y)^{0.5}$	$(Y)^{0.1}$
Slope ±SE‡		-0.0101	-0.098	-0.00591
		±0.0011	±0.021	±0.00086
Intercept ±SE		1.708	7.389	1.357
		±0.023	±0.449	±0.019
r^2		0.839	0.558	0.729
P		<0.00001	<0.0005	<0.00001

* mean ±1 standard deviation for samples collected on multiple cruises, † mean ±1 standard deviation (analytical error), ‡ standard error.

Table 2. Black carbon content of standard reference materials and natural organic matrices.

Material	%TOC	BC (g BC/g dry wt)	%BC/TOC
Diesel Particulate NIST SRM 1650	79.25 ±1.45*	0.5232 ±0.0028	66.02 ±0.35
Urban Dust NIST SRM 1649a	17.96 ±0.04	0.0407 ±0.0014	22.66 ±0.78
Suwannee River DOM IHSS 1R101N	44.81 ±1.16	0.0015 ±0.00013	0.335 ±0.029
Peat Humic Acid IHSS 1R103H	51.30 ±0.26	0.00030 ±0.00038	0.058 ±0.075
Isochrysis galbana	51.75 ±1.01	0.0121 ±0.0014	2.33 ±0.28
Skeletonema costatum	21.72 ±0.05	0.0102 ±0.0016	4.68 ±0.75
S. costatum detritus	18.93 ±0.31	0.00155 ±0.000007	0.819 ±0.004
S. costatum detritus†	18.93 ±0.31	0.00439 ±0.00038	2.32 ±0.20
Calcium carbonate‡	11.88 ±0.04‡	0.00024 ±0.00003	0.202 ±0.025‡

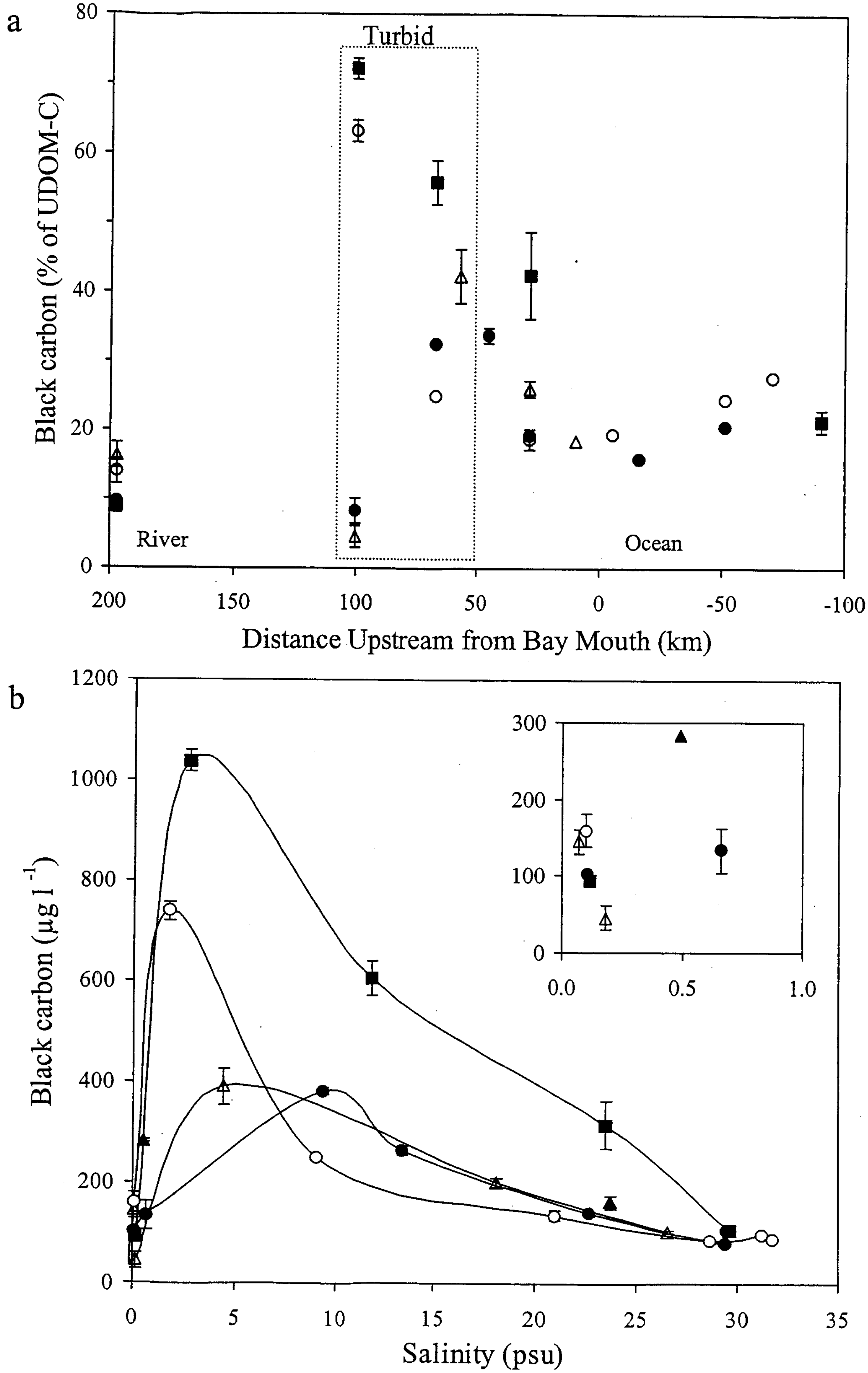
* mean ±1 standard deviation for triplicate or duplicate analyses, † thermal oxidation conducted after acid fuming, ‡ inorganic carbon – sample was not fumed with acid vapors.

Diesel particulate and urban dust are standard reference materials (SRM) obtained from the National Institute of Standards and Technology (NIST). Suwannee River DOM (dissolved organic matter) and peat humic acid are reference materials obtained from the International Humic Substances Society (IHSS). *Isochryis galbana* and *Skeletonema costatum* samples were collected from non-axenic and axenic phytoplankton cultures, respectively. *Skeletonema costatum* is the dominant bloom forming phytoplankton (diatom) in U.S. Mid-Atlantic coastal waters. *S. costatum* detritus is residual material from an experimental diatom bloom after >50 days of microbial degradation in darkness.

Table 3. Fluxes of black carbon and lignin phenols through DOM from Delaware Bay and global rivers to the ocean.

	Delaware Bay flux ($g\ yr^{-1}$)	Global river flux ($g\ yr^{-1}$)
Black carbon	2.4×10^{10}	5.5×10^{12}
Lignin	2.3×10^{8} (ref. 19)	0.76×10^{12}

Delaware Bay fluxes are based on a surface volume outflow of 8000 $m^3\ s^{-1}$ at the bay mouth[20] and an average coastal ocean UDOM black carbon concentration of 93.8 $\mu g\ l^{-1}$. Estimates of global river fluxes are based on a global river discharge of 35,300 $km^3\ yr^{-1}$ (ref. 21), average BC concentration in UDOM from the Delaware River and headwaters of Chesapeake Bay (156.4 $\mu g\ l^{-1}$), and an average lignin phenol concentration of 21.6 $\mu g\ l^{-1}$ for DOM from the Amazon and Mississippi rivers[22].



Mannino & Harvey, Figure 1

Supplementary Information – Not for Publication

Radiocarbon and stable carbon isotope measurements of black carbon residues from Delaware Bay and Chesapeake Bay UDOM. Radiocarbon measurements are not corrected for reservoir effects.

Cruise	Salinity	Distance (km)	NOSAMS* #	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Radiocarbon Age (yr bp)
June 1996	0.104	197	OS-31087	-25.11	405	>Modern
June 1996	9.36	66.4	OS-32047	nd†	23.7	Modern
June 1996	22.67	28.4	OS-29759	nd	201.3	Modern
June 1996	29.48	-51.5	OS-32058	nd	-64.2	485 ±140
Sept. 1996	2.72	100	OS-34423	-26.55	10.7	Modern
March 1997	4.44	56.6	OS-33789	-26.25	400.5	>Modern
March 1997	26.6	9.4	OS-33790	-23.41	276.3	>Modern
May-June 1997	0.099	197	OS-33063	-26.5	263.4	>Modern
May-June 1997	31.2	-51.5	OS-33342	-21.96	5273.7	>>Modern
May-June 1997	0.492	Chesapeake Bay headwaters	OS-34316	-25.98	79.9	Modern
May-June 1997	23.76	Chesapeake Bay coastal ocean	OS-33791	-46.22	-974.3	29,400 ±150

* National Ocean Sciences Accelerator Mass Spectrometry facility at Woods Hole Oceanographic Institute, † not determined.